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FLUORIDES AND OXYFLUORIDES
OF CHLORINE

Review Article

ATD Work Assignment No. 69

J. Kourilo

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FOREWORD

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This report, prepared in response to ATD Work Assignment No. 69, presents limited information gathered from Soviet open source materials available at the Aerospace Technology Division and the Library of Congress. It covers the period from 1958 through June, 1964. The materials are divided into two parts corresponding to the principal questions raised in the Work Assignment. The presentation of the pertinent materials is summarized in a comment by the analyst. A list of references arranged in alphabetical order by author is included at the end of the report. Arabic numerals in brackets inserted in the text are the sequence numbers from the list of references.

1 4

INTRODUCTION

The Work Assignment can be summarized in two fundamental questions raised in connection with a 1962 article by G. N. Bogachov [1]: 1) What is the real name for the "new compound - perftorkhlorid" mentioned in the article and why is it named "perftorkhlorid?" and 2) Are there any indications in the Soviet literature for higher fluorides of chlorine than trifluoride (ClF_3)? The following materials are designed to supply limited information which will provide the answers (see the Comment) to the above-formulated fundamental questions.

"New compound - perftorkhlorid"

With respect to inorganic fluorine compounds Russian scientists follow a dual terminology — Russian and international [5][20], because a generally adopted Russian chemical terminology is absent [20]. This dual approach is reflected in the names of the fluorine compounds with chlorine and oxygen [10][20] and with chlorine alone (fluorides of chlorine) [5][20]. The former, such as perchloryl fluoride, FClO_3 , and fluorine perchlorate, FClO_4 , are designated indiscriminately as "perkhlorilftorid" [10][20], "khloratftora" [20], "khloriloksiftorid" [20] for FClO_3 , or "perkhlorat ftora" [20], "perkhloriloksiftorid" [20] for FClO_4 . The fluorides of chlorine are classified either as "galogenidy khlor" [5] [halides of chlorine] on the basis of their chemical composition, or as "ftoridy galogenov" [5] [20] [fluorides of halogen] on the basis of the nature of the more electropositive element. Thus, chlorine monofluoride, ClF , and chlorine trifluoride, ClF_3 , are named "ftoristyy khlor" [5][20] or "monoftorid khlor" [19][22], and "trekhftoristyy khlor" [4][5][10][16][20] or "triftorid khlor" [1][3][17][18][19][22], respectively. Often a Soviet author in the same article [10] or in two different articles [16][17] indiscriminately uses both names for the same fluoride of chlorine. However, a marked preference toward the "fluorides of halogen" terminology is noticeable in the 1960-62 publications [3][17][18][19][22] but not in the earlier [5][16] or later [4][10] ones.

Russian scientists use such expressions as "higher forms" [5], "higher halides of chlorine" [5], "higher fluorides" [22], or "dimer" [5][22] (see page 3 below) for higher fluorides of chlorine than ClF . However, one source [4] describes chlorine pentafluoride as "pyatiftoristyy khlor." Bromine pentafluoride, iodine pentafluoride, and iodine heptafluoride are commonly referred to as "pyatiftoristyy brom" [5][10][20], or "pentaftorid broma" [3], "pyatiftoristyy iod" [5][8], and "semiftoristyy iod" [5][8][20], respectively. The names "perftorid khlor" or "broma" or "ioda" for higher fluorides of halogen were not found in any Soviet publication. The prefix "perftor" attached to the name of the basic unsubstituted compound is used as a rule for naming certain fluoro-organic compounds [8][9][11][12][13][14][15]. This prefix was encountered in the Soviet name of only one inorganic fluorine compound - tetrafluorhydrazine, which is sometimes called "perftorgidrazin" [7].

In the investigation of the source of Bogachov's information on the "perftorkhlorid" a reference in his article to an American Source [23] was evaluated. Excerpts from a paragraph on p. 37 of this source are quoted below, alongside the translated sentence from p. 40 of Bogachov's article.

American Source [23], p. 37:
 "Others. There are many
fluorides which are sold only
in very small quantities....
Owing to its high dielectric
strength, sulfur hexafluoride
is being used on a limited
scale as a gaseous insulator
for electrical equipment.
Perchloryl fluoride is a
rather interesting new chem-
ical.... Chlorine trifluoride
is finding use in oil well
drilling operations...consump-
tion of stannous fluoride is
actually very small...."

Bogachov article [1], p. 40:
 "Among other fluorides, small
quantities of sulfur hexa-
fluoride (as a gaseous in-
ulator with high dielectric
properties), chlorine triflu-
oride, which is used in drill-
ing operations, stannous flu-
oride, and a new compound -
"perftorkhlord" -- are produced."

Three other references in Bogachov's article were found helpful in evaluating the author's background and in projecting light on his chemical terminology. One of them [2] is the reference to a textbook by G. N. Bogachov written for foremen of the metal fluorides industry. The book deals with the technology of manufacturing fluorine salts. Two other books by G. N. Bogachov, which are listed as references 11 and 12 to his article, are not available at the Library of Congress or ATD. The first book deals with the technology of chromium and fluorine salts and the second with chemical raw materials in the [Soviet] Far East. Otherwise, not a single article by G. N. Bogachov could be found anywhere in the Soviet literature covered in this report.

Higher Fluorides Of Chlorine

Information concerning the existence of higher fluorine compounds with chlorine is very scarce. As late as 1960 a Soviet source [22] even claimed "an insufficient knowledge of ClF_3 , the chemical properties of which are little known." However, the same source reported that "the ClF_3 - Cl_2 and ClF_3 - ClF systems were studied" but without results. An earlier (1956) Soviet monograph [20] noted only that " ClF_3 mentioned in a Western source is a misprint." Ya. A. Fialkov, a noted Soviet chemist and Corresponding Member of the Academy of Sciences UkrSSR [21] described in his 1958 monograph [5] all 12 known (up to mid-1956) interhalogen compounds not counting the corresponding ionic forms [5][6] and dimers. The highest fluoride of chlorine known at that time was ClF_3 . The same author reported (p. 29) that according to literature a mixture of ClF and ClF_3 is formed in the reaction of chlorine with an excess of fluorine [presumably, an

excess over stoichiometric ratio in ClF_3]; also that FCl_2 , reacting with chlorine is reduced to FCl (p. 198). The causes of nonexistence or considerable instability of higher molecular (ClF_5 and ClF_7) or ionic forms (ClF_4^-) of fluorine-chlorine compounds are discussed in the same monograph (pp. 323-332). Nevertheless, the author cautiously assumes that " ClF_3 is able to react with all elements, except inert gases, oxygen, nitrogen, and perhaps P" (p. 38), and that " ClF_3 reacting with fluorine is oxidized to possible higher forms" (p. 198). The later Soviet sources evaluated refer to chlorine trifluoride only as the most powerful fluorinating agent [18] or the most suitable liquid oxidizer in rocket fuel [10] and fail to mention any higher fluorides of chlorine. It is also noteworthy that perchlorylfluoride is named as a very promising, excellent oxidizer for oxygen and carbon-containing fuels [10], and American production of FClO_2 for rocket fuels is reported [14]. The first and unique positive indication for higher than FCl_2 fluoride of chlorine was found in a 1964 Soviet source [4] which reports a note in the British periodical "Science" (v. 141, 1963, p. 1039) on the preparation by an American chemist of a new compound — chlorine pentafluoride ("pyatiftoristyy khlor") from chlorine trifluoride and fluorine under high pressure.

The existence of a dimeric molecular form of ClF_3 — $(\text{ClF}_3)_2$ in the gas phase at low temperature is reported by Ya. A. Fialkov [5] from a 1947 German source and confirmed later [22]. This form is referred to as "dimer."

Comment

It seems clear from the evaluation of the above presented materials that the "new compound — perftorkhlorid" in the Bogachov article is perchloryl fluoride, mentioned in the American source [23]. The whole sentence in the Bogachov article including the name "perftorkhlorid" is a paraphrased paragraph from the American source (see p. of this report). It is, therefore, certain that the "new compound" is of American origin. The answer to the question of why perchloryl fluoride was translated as "perftorkhlorid" and not given one of the usual Soviet names given near the beginning of this report may be found in the background of the author. G. N. Bogachov's name is virtually unknown in the Soviet scientific literature; his works attest to an engineering background with a rudimentary knowledge of chemistry and chemical terminology.

Information collected from the Soviet open literature does not make it possible to answer one way or another the question of whether higher fluorides of chlorine than ClF_3 were prepared or are being produced in USSR. Even a 1963 Soviet source [25] mentioned chlorine trifluoride as the highest of halogen fluorides in connection with rocket fuels. The 1963 Western acknowledgment of the chlorine pentafluoride discovery was duly reported in a Soviet periodical but without comment.

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